



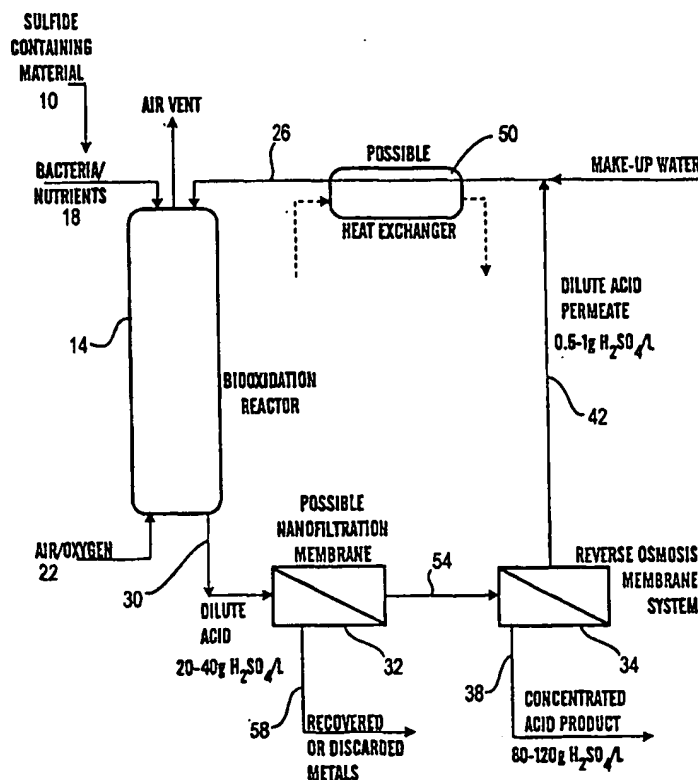
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C01B 17/74, 17/90, C02F 1/44, B01D 61/00		A1	(11) International Publication Number: WO 00/50341
			(43) International Publication Date: 31 August 2000 (31.08.00)
(21) International Application Number: PCT/US00/04632		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 23 February 2000 (23.02.00)		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(30) Priority Data: 60/121,267 23 February 1999 (23.02.99) US			
(71) Applicant (for all designated States except US): HW PROCESS TECHNOLOGIES, INC. [US/US]; 1201 Quail Street, Lakewood, CO 80215 (US).			
(72) Inventors; and (75) Inventors/Applicants (for US only): GREEN, Dennis, H. [US/US]; 9455 West 68th Avenue, Arvada, CO 80004 (US). MEULLER, Jeff [US/US]; 3462 Cripple Creek Square, Boulder, CO 80303 (US).			
(74) Agents: SWARTZ, Douglas, W. et al.; Sheridan Ross P.C., Suite 1200, 1560 Broadway, Denver, CO 80202-5141 (US).			

(54) Title: METHOD OF ACID CONCENTRATION FOLLOWING BIOLOGICAL OXIDATIVE GENERATION OF SULFURIC ACID FROM SULFIDES

(57) Abstract

The process of the present invention is a sulfide or sulfur bio-oxidation process (14) in which the sulfuric acid is recovered from a bio-oxidation solution (30) through filtration. The bio-oxidation solution is base metal impurity cleaned using a membrane filter (32) and the acid is recovered, preferably using a membrane filter (34). The acid lean solution (42) is recycled to the bio-oxidation reactor (14) to manufacture more sulfuric acid.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

METHOD OF ACID CONCENTRATION FOLLOWING BIOLOGICAL OXIDATIVE GENERATION OF SULFURIC ACID FROM SULFIDES

5

FIELD OF THE INVENTION

The process of the present invention is directed generally to sulfuric acid production processes and specifically to a sulfuric acid production process recovering the acid using filtration techniques.

10

BACKGROUND

The sulfuric acid consumptive heap leach-solvent extraction-electrowin (SX-EW) copper cathode production process, one of the fastest growing sectors of the global mining industry, displaces a proportionate amount of mineral concentrate smelting for the recovery of copper. Smelting has historically produced a large percentage of the sulfuric acid used in the mining industry. The resultant reduced level of smelting leads to a reduced supply of smelter by-product sulfuric acid.

Coincidental with the increase in the use of the sulfuric acid consumptive SX-EW and reduction of by-product sulfuric acid, there has been an increase in the number of sulfuric acid by-productive biohydrometallurgical technologies available to mines. This biohydrometallurgically produced acid is a logical candidate to replace the acid no longer produced by the smelters.

The acid produced by biohydrometallurgical processing, however, is often unfit for use by mines. The acid is typically metals loaded, *i.e.*, contaminated with dissolved and dissociated zinc, iron, copper, and arsenic, among other things, in accordance with the metals content of the feedstock and nutrient and additives used to promote the bio-oxidation of the feedstock. These metals in combination with the increased acidity accruing to the progression of the biohydrometallurgical process, will accumulate over time and reuse unit they constitute a fouled, or toxic (for the bacteria), solution that cannot be reused in the source bioprocess. As a result, metallurgical processes must discard the fouled sulfuric acid solutions and use fresh sulfuric acid purchased from a supplier at high cost. The fresh sulfuric acid represents a significant operating cost for mines, particularly for mines in remote locations.

SUMMARY OF THE INVENTION

The various embodiments of the present invention address these and other needs as is apparent from the following disclosure.

5 The process of the present invention manufactures sulfuric acid through bio-oxidation techniques. The process uses one or more filtration processes to remove dissolved impurities, such as dissolved and dissociated metals, chlorides, nitrates, and the like, from the raw sulfuric acid-containing product of the process.

In one embodiment, the process includes the steps of:

10 (a) contacting a sulfide-containing feed material with bacteria and oxygen to produce sulfuric acid in the form of an acid-containing solution; and

(b) filtering at least a portion of the acid-containing solution to form a retentate and a permeate, the retentate containing at least most (typically at least about 90%) of the multivalent metal impurities and some sulfuric acid (typically no more than about 25%) and the permeate containing at least most (typically at least about 75%) of the sulfuric acid.

15 The impurities can be multivalent, dissociated ions, such as copper, iron, zinc, nickel, manganese, and other metals from Group IIA of the Periodic Table of the Elements. In one configuration, the pore size and electric charge of the filter is selected to retain at least most of the multivalent metals in the retentate and pass at least most (typically at least about 65%) of the monovalent compounds, such as sulfuric acid.

20 Alternatively, the impurities can also be both multivalent and monovalent. Examples of monovalent impurities include nitrates, and chlorides, which are typically compounded with monovalent metals from Groups IA and IIA of the Periodic Table of the Elements. In one configuration, the filter is selected to pass at least most (typically at least about 65%) of the monovalent impurities while retaining at least most (typically at least about 65%) of the sulfuric acid.

25 The process can include additional filtration steps. By way of example, the permeate can be filtered to produce a second retentate and second permeate. In one configuration, at least most of any remaining metals and at least most of the sulfuric acid in the permeate are contained in the second retentate. The sulfuric acid concentration in the second retentate is more than the sulfuric acid concentration in the second permeate. 30 The second permeate can be recycled to step (a) for use in producing more sulfuric acid.

The process promotes rapid bio-oxidation rates by maintaining the acid concentration in the second permeate at low levels through the removal of excess acid in the second filtering step, thereby promoting bacterial production of more sulfuric acid. The process also permits sulfuric acid produced on site in biohydrometallurgical mining processes to
5 be reused in bio-oxidation at a considerable cost savings to the mine operator and/or sold at a substantial profit as a byproduct.

The bio-oxidation reaction in step (a) can be performed in a suitable reactor or in a heap or pile of the sulfide-containing material. Examples of suitable reactors are trickle bed reactors, continuous stirred or air sparged, agitated reactors, and open air piles.

10 Most of the acid in the acid-containing solution preferably reports to the permeate and later to the second retentate. The acid-containing solution typically has an acid content ranging from about 5 to about 50 g/l. The acid concentration in the retentate is typically the same as the acid concentration in the permeate because the acid readily passes through the first filter. Because the permeate represents a larger volume than the
15 retentate, the permeate typically contains more of the acid in the solution than the retentate. The second retentate preferably includes at least about 50 and more preferably from about 75 to about 97% of the acid in the acid-containing solution while the second permeate preferably has no more than about 50% and more preferably from about 10 to about 15% of the acid in the acid-containing solution. The second retentate typically has
20 an acid concentration of at least about 100 g/l acid. The second permeate typically has an acid concentration of no more than about 5 g/l acid and more typically ranging from about 0.1 to about 2 g/l acid.

In one configuration, the first filter preferably has a larger pore size than the second filter such that the sulfuric acid (but not multivalent metal impurities) passes
25 through the first filter. The sulfuric acid and any remaining impurities are retained by the second filter.

In another configuration, the first and second filters are preferably a nanofilter membrane, a reverse osmosis membrane, and combinations thereof. The first filter preferably has a pore size ranging from about 20 to about 100 angstroms. The second
30 filter preferably has a pore size ranging from about 1 to about 20 angstroms.

In the first filtering step, the permeate preferably constitutes at least most of the volume of the acid-containing solution. The permeate preferably constitutes at least about 50 and more preferably from about 80 to about 90% by volume of the acid-containing solution while the retentate preferably constitutes from about 20 to about 10% by volume of the solution.

In the second filtering step, the second permeate preferably also constitutes at least most of the volume of the acid-containing solution. The second permeate preferably constitutes at least about 50 and more preferably from about 80 to about 90% by volume of the acid-containing solution while the second retentate preferably constitutes from about 20 to about 40% by volume of the solution.

The process can include additional steps to remove dissolved multivalent metal impurities such as arsenic, copper, iron, nickel, calcium, magnesium, manganese and other di- and tri- valent metal ions, or metal ion complexes from the first and/or second retentate. The metal can be recovered by precipitation, electrolysis, ion exchange resins, cementation, and solvent extraction.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow schematic depicting a first embodiment of the process; and Figure 2 is a flow schematic depicting a second embodiment of the process.

20

DETAILED DESCRIPTION

A first embodiment of a process according to the present invention is directed to the bio-oxidation of a sulfide-containing material to form sulfuric acid, and more particularly to enhanced production of sulfuric acid using an acid-resistant, nanofiltration membrane to remove multivalent impurities and an acid-resistant, reverse osmosis membrane process to concentrate sulfuric acid for sale in a second retentate, while permeating a lean acid solution for return to the bacterial sulfuric acid production step. The acid rich or concentrated acid product is a dilute (10-50 g H₂SO₄/L) sulfuric acid produced by bio-oxidation of the sulfur component of the sulfidic material. This process improves the value of the product from the bacterial sulfuric acid production step, and

30

may enhance the production process by continually removing a portion of the sulfuric acid, thus accelerating or assisting the further bacterial production of sulfuric acid.

Referring to Figure 1, a sulfide-containing material or sulfide-coated substrate 10 are placed in a vat or column reactor 14 (or pile), inoculated with bacteria and bacteria nutrients 18. The bacteria can be any suitable bacteria, such as *Thiobacillus* bacteria (e.g., *Thiobacillus Ferroxidans*, *Thiobacillus Thiooxidans*, etc.), *Leptospirillum Ferroxidans*, *Sulfobacillus Thermosulfidooxidans*, *Sulfolobus* bacteria, and/or *Acidiamus*. The nutrients are typically ammonium sulfate (e.g., from about 0.1 to about 0.5 gpl), phosphate (e.g., about 40 ppm), and iron (e.g., from about 0.4 to about 30 gpl of Fe^{+3}), carbon and oxygen. The material 10 is sprayed with or immersed and/or stirred in dilute (e.g., about 1-2 g $\text{H}_2\text{SO}_4/\text{L}$) acid 26 and sparged with air. After a period of time, the sulfuric acid concentration of the solution grows to the range of about 20-40 g $\text{H}_2\text{SO}_4/\text{L}$ due to the bio-oxidation process. This product solution 30 is then passed through acid-resistant membrane systems 32 and 34 to produce an acid concentrate stream 38, i.e. membrane concentrate, of about 50-120 g $\text{H}_2\text{SO}_4/\text{L}$, and an acid lean stream 42, i.e. membrane permeate, of about 0.5-1 g $\text{H}_2\text{SO}_4/\text{L}$. The membrane concentrate 38 is collected in a tank for sale as product; the membrane permeate 42 is returned to the reactor or pile for further bio-oxidation acid production. The membrane process provides a way to upgrade the dilute acid to provide a superior saleable acid product.

As will be appreciated, the membrane systems 32 and 34 can each be configured as a single membrane or multiple membranes. The multiple membranes can treat the feed stream serially and/or in parallel.

Bio-oxidation of sulfides for production of sulfuric acid is accomplished by using a suitable bacteria. Air, oxygen and trace nutrients can continually or intermittently be added to the recycled solution to speed the kinetics of this bio-oxidation process. As noted, the commercial process would involve placing a sulfide-containing material or sulfide coated substrates, in a vat, column, tank, or freestanding pile or heap. The sulfide is then inoculated with bacteria, nutrients, and air, and sprayed with or immersed in dilute (1-2 g $\text{H}_2\text{SO}_4/\text{L}$) acid. The solution is recirculated and oxygen or air may be blown, diffused or bubbled into the solution, and, after a period of time (typically 1-4 weeks), sulfuric acid concentration of the solution grows to the range of about 20-40 g $\text{H}_2\text{SO}_4/\text{L}$.

The sulfur component of the sulfide-containing material is slowly consumed during the acid generation process.

As the bacteria oxidation process can generate significant heat, particularly in a column reactor, a heat exchanger 50 may be needed to remove this heat. A typical shell and tube heat exchanger would be sufficient with heat being transferred from the
5 regulating acid situation to process water or make-up water.

The bio-oxidation rate of acid production is affected by the concentration of acid in the column, tank, or heap, and the air or oxygen availability, nutrient availability, temperature, and contaminant metal concentrations (if any). These variables may conspire
10 to optimize bio-oxidation production of sulfuric acid at a sulfuric acid concentration of about 20-40 g H₂SO₄/L. This acid concentration, approximately 2-4%, is fairly dilute, and thus limits the uses for this inexpensively produced acid product. For example, dilute acid such as this may add substantial water to the process, which often creates water balance problems. Also, many processes, such as electrowinning tankhouses, require
15 more concentrated acid addition, in the 100-200 g H₂SO₄/L (10-20 wt% range).

Another limitation or adverse effect on production and final product value is the presence of small or significant quantities of heavy metals or other ion impurities. Sulfuric acid is priced according to grade, with "technical grade" containing certain impurities and selling for less than "food grade", which contains less impurities. Also, certain impurities,
20 such as arsenic, may be toxic or inhibitory to the sulfuric acid producing bacteria, and slow or stop the bio-oxidation process, resulting in a corresponding drop in rate of acid production.

The process of the present invention improves the bio-oxidation process by using the membrane system 34 to remove and concentrate acid, while maintaining the rate of
25 biooxidation at its peak. This provides a wider ranging market and more saleable sulfuric acid product. Accordingly, the invention represents an advance in the art of bio-oxidation of sulfides to sulfuric acid, as described in detail herein.

The process improvements claimed in the present invention will result from utilizing an acid-resistant reverse osmosis membrane system 34 and acid-resistant
30 nanofiltration membrane system 50 to purify and concentrate the dilute sulfuric acid product from bio-oxidation of sulfides. As described above, the use of a membrane

process to remove and concentrate acid allows the bio-oxidation reactor to be run at maximum rate of acid production.

In the improved process shown in Figure 1, the dilute sulfuric acid product is passed through the reverse osmosis membrane system 34, after first passing through a nanofiltration membrane system 32 (to remove dissolved and dissociated multivalent metal impurities). The dilute acid solution is first sent to the acid-resistant nanofiltration membrane 50 which separates the solution into two streams-permeate 54 and concentrate 58. During this step, the osmotic pressure preferably ranges from about 150 to about 1,000 psi. The permeate 54 is greatly reduced in multivalent impurity concentration, containing a minority of the impurities. Acid concentration is approximately the same in the permeate and the concentrate, only divalent and trivalent ion impurities such as iron and copper are rejected and concentrated in the membrane concentrate. The impurity clean permeate 54 is sent to the reverse osmosis membrane 34 for concentration. The reverse osmosis membrane separates the acid into two streams: permeate 42 and concentrate or retentate 38. During this step, the osmotic pressure preferably ranges from about 150 to about 1,000 psi. The permeate 42 is greatly reduced in acid concentration, and is returned to the bio-oxidation reactor. The concentrate 38 is greatly increased in acid concentration, and it is collected for sale.

The concentrate 58 is greatly increased in impurity concentration, containing a majority of the impurities. The concentrate 58 may be removed from the sulfuric acid processing system and the metals recovered and/or disposed of through neutralization and precipitation.

The reverse osmosis membrane system 34 of the first embodiment would process 10 -10,000 gallons per minute of dilute sulfuric acid solution, with 65-95% of the feed flow becoming permeate product. Typical reverse osmosis membranes used would be S or A series elements from Osmonics/Desalination Systems of Vista, CA. For example, SC, SE, SG, AD, AG, AK membrane elements are appropriate. A typical system would process 1000 gpm of 20 g $\text{H}_2\text{SO}_4/\text{L}$ sulfuric acid solution through 600 each 8 inch diameter, 40 inches long spiral wound SE membrane elements, at 600-800 psi and 30-40 deg C. The system would split the feed flow into 800 gpm of permeate containing about 0.5 g $\text{H}_2\text{SO}_4/\text{L}$, and 200 gpm of concentrate containing about 98 g $\text{H}_2\text{SO}_4/\text{L}$. The

concentrate would be collected and sold as a high grade sulfuric acid product. The permeate would be returned to the bio-oxidation reactor 14.

The nanofiltration membrane system 32 of the first embodiment would process 10-10,000 gallons per minute of dilute sulfuric acid solution, with 50-95% of the feed flow becoming permeate product. The typical nanofiltration membrane used would be D or G series elements from Osmonics/Desalination Systems of Vista, CA. For example, DK, DL, GE, GH membrane elements are appropriate. A typical system would process 1000 gpm of 20 g $\text{H}_2\text{SO}_4/\text{L}$ sulfuric acid solution, containing 1 g iron/L, through 500 each 8 inch diameter, 40 inches long spiral wound DK membrane elements, at 200-400 psi and 30-40 deg C. The system would split the feed flow into 800 gpm of permeate containing about 20 g $\text{H}_2\text{SO}_4/\text{L}$ and 0.01 g iron/L, and 200 gpm of concentrate containing about 20 g $\text{H}_2\text{SO}_4/\text{L}$ and 5 g iron/L. The concentrate 58 would be sent to a precipitation system or ion exchange system for iron removal. As above, the permeate 54 would be sent to the reverse osmosis membrane system for acid concentration.

A second embodiment of the present invention is depicted in Figure 2. Referring to Figure 2, a sulfide-containing material or a sulfide coated substrate 10 is placed in a reactor or pile 14, inoculated with bacteria and bacteria nutrients 18, sparged with air 22, and sprayed with or immersed in dilute sulfuric acid 26. A product solution 30 is withdrawn and passed through a first membrane filter system 32 to form a first retentate 58 containing at least most of the multivalent impurities and a first permeate 54 containing at least most of the sulfuric acid and selected monovalent impurities, typically nitrates and chlorides. The first permeate 54 is passed through a second membrane filter system 100 to form a second permeate 108 containing at least most (typically at least about 65%) of the nitrates and chlorides in the first permeate 54 and a second retentate 104 containing at least most (typically at least about 65%) of the sulfuric acid in the first permeate 54. The second permeate 108 can be discarded. A portion 102 of the second retentate 104 can be combined with the make-up water 112 and recycled to the reactor or pile 14. The remaining portion 110 of the second retentate 104 can be further concentrated, if necessary, by a reverse osmosis filter system 118 for sale as a product 122. The permeate 124 of the reverse osmosis process 118 can be combined with make-up water 112 for reuse.

The preferred membrane in the second filter system 100 is a G series ultrafilter manufactured by Osmonics. Chlorides and nitrates are preferentially passed through this membrane relative to sulfuric acid and the chloride to sulfuric acid and nitrate to sulfuric acid ratios of the second retentate of the G series ultrafilter are reduced. The molar ratios of nitrate to acid and of chloride to acid typically are reduced from a range of from about 0.25:1 to about 5:1 to a range (in the second retentate) of from about 0.01:1 to about 2.5:1.

The various membranes discussed above are further discussed in U.S. Patents 5,476,591, 5,310,486, and 5,116,511 to Green et al.; U.S. Application Serial No. 08/871,176, filed June 9, 1997; U.S. Application Serial No. 09/052,869, filed March 31, 1998; U.S. Application Serial No. 09/183,683, filed October 30, 1998; U.S. Application No. 60/121,267, filed February 23, 1999, and U.S. Application 09/342,338, filed June 29, 1999, all of which are incorporated herein by this reference.

15

Example

A solution of dilute sulfuric acid produced by bio-oxidation of sulfur was concentrated using a SE1812 spiral wound membrane filter. The pressure was held at 600 psi, and the temperature was held at 24-25 deg C. This gave a flux rate of about 6 gfd through 65% recovery. Samples of feed, composite concentrate and permeate were taken at 65% recovery and 80% recovery. Feed, concentrate, and permeate acid concentrations were measured by titration With a 0.05 g NaOH/mL solution. 50 mL of sample was used, and 10 drops of phenolphthalein was used to determine the titration endpoint. Overall membrane rejection performance results are shown in Table 1. Acid rejection was generally very good under these conditions. Permeate quality declined gradually from 65 to 80% recovery, but acid rejection was still above 95% at 80% recovery.

Table 1 Bench Test Acid Concentration Results

Test	Feed*	Concentrate*	Permeate*
R/O Membrane			
-65% recovery	16.4	46.6	0.12
% Rejection (1-p/f)			99.3
% Balance		AR=65%	100
-80% recovery		73.5	0.37
% Rejection (1-p/f)			97.7
% Balance		AR=78%	91.4

* g H₂SO₄/L

AR = adjusted recovery to get 100% material balance.

The foregoing description of the acid concentration component of the present invention has been presented for purposes of illustration and description. Furthermore, the description is not intended to limit the invention to the form disclosed herein. Consequently, variations and modifications commensurate with the above teachings, and the skill or knowledge of the relevant art, are within the scope of the present invention. The embodiments described hereinabove are further intended to explain best modes known for practicing the invention and to enable others skilled in the art to utilize the invention in such, or other, embodiments and with various modifications required by the particular applications or uses of the present invention. It is intended that the appended claims be construed to include alternative embodiments to the extent permitted by the prior art.

What is claimed is:

1. A process for manufacturing sulfuric acid, comprising:
 - (a) contacting a sulfide-containing feed material with a bacteria and oxygen to form a sulfuric acid solution having a first concentration of sulfuric acid and impurities;
 - 5 (b) filtering at least a portion of the sulfuric acid solution to form a retentate containing at least most of the impurities and a permeate containing at least most of the sulfuric acid in the sulfuric acid solution;
 - (c) filtering at least a portion of the permeate to form a second retentate having a second sulfuric acid concentration that is greater than the first concentration and
10 a second permeate having a third sulfuric acid concentration that is less than the first concentration; and
 - (c) recycling at least a portion of the second permeate to step (a) to form additional sulfuric acid.
2. The process of Claim 1, wherein the second retentate has an acid
15 concentration of at least about 100 g/l of the acid.
3. The process of Claim 1, wherein the second permeate has an acid concentration of no more than about 5 g/l of the acid.
4. The process of Claim 1, wherein the second retentate contains at least most of an acid in the solution.
- 20 5. The process of Claim 1, wherein the second retentate includes at least about 90% of the acid in the solution.
6. The process of Claim 1, wherein the second permeate includes no more than about 10% of the acid in the solution.
7. The process of Claim 1, wherein the filtering steps (b) and (c) are each
25 performed using at least one of a nanofilter membrane, a reverse osmosis membrane, and combinations thereof.
8. The process of Claim 7, wherein the reverse osmosis filter has a pore size of no more than about 20 angstroms.
9. The process of Claim 1, wherein the second retentate constitutes from
30 about 50 to about 85% by volume of the solution.

10. The process of Claim 1, wherein the nutrients are selected from the group consisting of phosphorous, nitrogen, iron, and mixtures thereof.
11. The process of Claim 1, wherein the temperature of the bio-oxidation reaction is maintained from about 20 to about 80 °C.
- 5 12. The process of Claim 1, wherein in step (a) the feed material is further contacted with a feed solution containing from about 1 to about 100 g/l sulfuric acid.
13. The process of Claim 1, wherein the multivalent metal is selected from the group consisting of iron, copper, nickel, arsenic, calcium, and mixtures thereof.
14. A method for producing sulfuric acid, comprising:
- 10 (a) contacting a sulfide-containing material with bacteria and oxygen to form a sulfuric acid solution having a first concentration of sulfuric acid and containing a monovalent impurity; and
- (b) filtering at least a portion of the solution to form a retentate having a second sulfuric acid concentration that is greater than the first concentration and a
- 15 permeate having a third sulfuric acid concentration that is less than the first concentration and wherein at least most of the monovalent impurity is in the permeate.
15. A process for manufacturing sulfuric acid, comprising:
- (a) contacting a sulfide-containing feed material with a bacteria and oxygen to form a sulfuric acid solution having a first concentration of sulfuric acid and impurities;
- 20 (b) filtering at least a portion of the sulfuric acid solution to form a retentate containing at least most of the impurities and a permeate containing at least most of the sulfuric acid in the sulfuric acid solution; and
- (c) recycling at least a portion of the permeate to step (a) to form additional sulfuric acid.

1/2

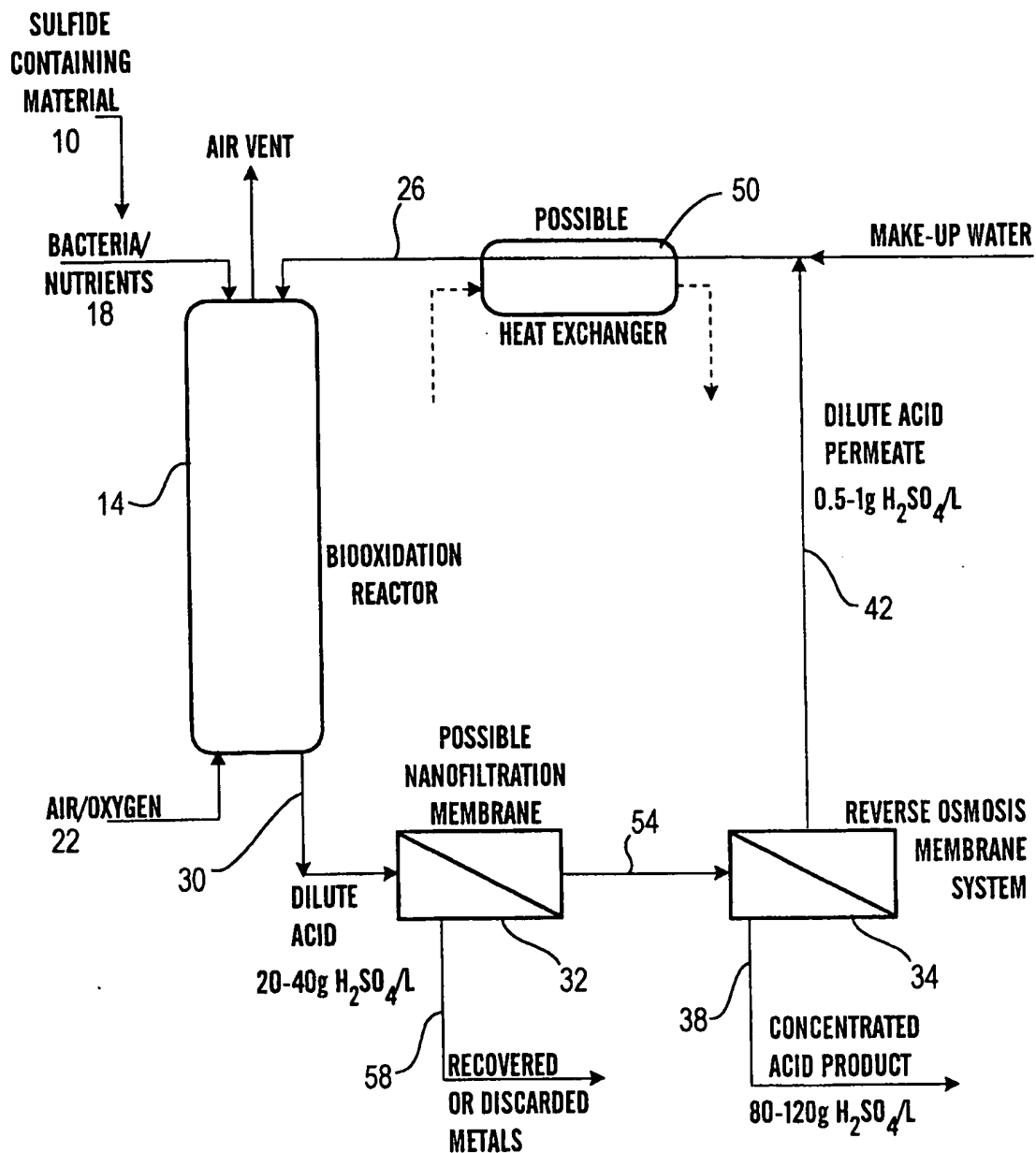


FIG. 1

2/2

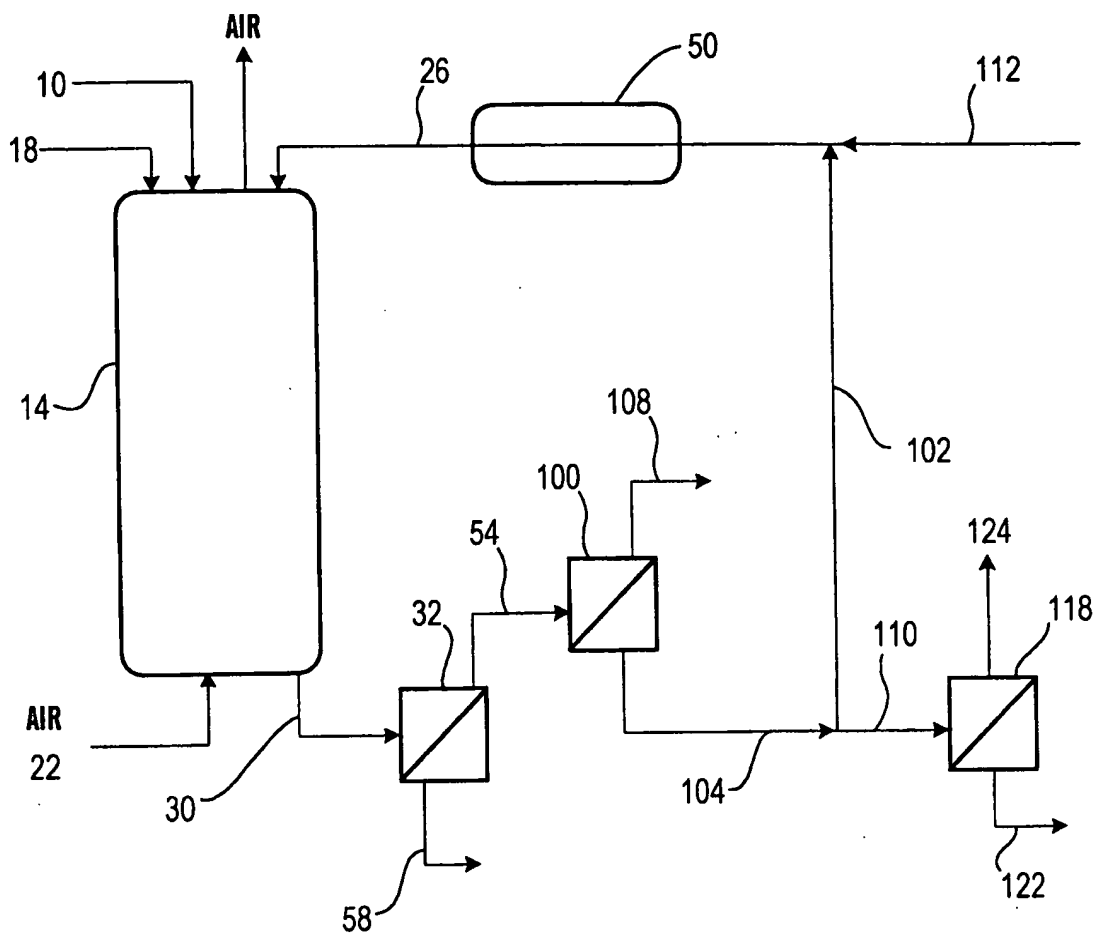


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/04632

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :CO1B 17/74, 17/90; CO2F 1/44; B01D 61/00

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/522, 531, digest 2, digest 17; 435/282, 821; 210/ 622,651, 652

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,E	US 6,056,934 A (CARLSEN et al) 02 May 2000, claim 1, column 5, lines 10-20	1-15
Y,E	US 6,031,158 A (MILLER et al) 29 FEBRUARY 2000, column 1, lines 40-60, column 5, lines 45-64	1-15
Y	US 5,779,762 A (KOHHR et al) 14 July 1998, abstract, claims 1 and 2	1-15
Y	US 5,476,591 A (GREEN) 19 December 1995, claim 9	1-15
A	US 5,587,083 A (TWARDOWSKI) 24 December 1996	1-15
A	US 5,403,490 A (DESAI) 04 April 1995	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

26 MAY 2000

Date of mailing of the international search report

05 JUL 2000

Name and mailing address of the ISA/US
Patent Office (as of the date of the report)
Box PCTAuthorized officer
Telephone No. (703) 308-0661DEBORAH THOMAS
PARALEGAL SPECIALIST

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/04632

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,246,486 A (BIERLEY et al) 21 September 1993	1-15
A,P	US 5,895,832 A (ECCLES) 20 April 1999	1-15
A	TUOVINEN ET AL., Use of Microorganisms for the Recovery of Metals, International Metallurgical Reviews, 1974, volume 9, pages 21-30	1-15
Form PCT/ISA/210 (continuation of second sheet) (July 1998)*		

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/04632

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

423/522, 531, digest 2, digest 17; 435/282, 821; 210/ 622,651, 652